

Efficiency of a Multi-Reference Coupled Cluster method

E. Giner,¹ G. David,² A. Scemama,^{2, a)} and J. P. Malrieu²

¹⁾*Dipartimento di Scienze Chimiche e Farmaceutiche,
Università di Ferrara, Via Fossato di Mortara 17,
I-44121 Ferrara, Italy*

²⁾*Laboratoire de Chimie et Physique Quantiques (CNRS 5626), IRSAMC, Université P. Sabatier,
Toulouse (France)*

The multi-reference Coupled Cluster method first proposed by Meller *et al* (*J. Chem. Phys.* 1996)¹ has been implemented and tested. Guess values of the amplitudes of the single and double excitations (the \hat{T} operator) on the top of the references are extracted from the knowledge of the coefficients of the Multi Reference Singles and Doubles Configuration Interaction (MRSDCI) matrix. The multiple parentage problem is solved by scaling these amplitudes on the interaction between the references and the Singles and Doubles. Then one proceeds to a dressing of the MRSDCI matrix under the effect of the Triples and Quadruples, the coefficients of which are estimated from the action of \hat{T}^2 . This dressing follows the logics of the intermediate effective Hamiltonian formalism. The dressed MRSDCI matrix is diagonalized and the process is iterated to convergence. The method is tested on a series of benchmark systems from Complete Active Spaces (CAS) involving 2 or 4 active electrons up to bond breakings. The comparison with Full Configuration Interaction (FCI) results shows that the errors are of the order of a few milli-hartree, five times smaller than those of the CASSDCI. The method is totally uncontracted, parallelizable, and extremely flexible since it may be applied to selected MR and/or selected SDCI. Some potential generalizations are briefly discussed.

I. INTRODUCTION

In the domain of molecular physics and quantum chemistry the many-body problem is perfectly clear as long as it is formulated from a single reference. The perturbative expansion of the wave operator and its diagrammatic transcription offer a guide to understand the relations between the multiplicative structure of the wave function and the additive structure of the energy. The linked cluster theorem² clarifies the questions of the size consistency and of the strict separability into fragments. The defects of truncated Configuration Interaction (CI) are well understood and algorithms have been proposed to respect approximately (CEPA-0^{3,4}, CEPA- n ⁵⁻⁷), or strictly ((SC)²CI)⁸ the cancellation of unlinked diagrams. The Coupled Cluster (CC) method⁹⁻¹¹ is definitely the most elegant formalism and can be considered as the standard treatment in its CCSD version, or in the CCSD(T) version¹² which incorporates the fourth order effect of the triply excited determinants. But all these approaches fail when one cannot expect that a single determinant will represent a reliable starting point to conveniently generate the wave function.

This is precisely the situation in many domains. The excited states present an intrinsic multi-determinantal character, and frequently a multi-configurational character. So are the magnetic systems in their low energy states, and the treatment of chemical reactions, in which chemical bonds are broken, also requires to consider geometries for which a single determinant picture is not relevant. A generalized linked cluster theorem has been established by Brandow¹³, which gives a con-

ceptual guide, but the conditions that must be fulfilled for its demonstration (Complete Active Space (CAS) as reference space, mono-electronic zero-order Hamiltonian) would lead to strongly divergent behaviors of the corresponding perturbative expansion in any realistic molecular problem. Practical computational tools have been proposed, most of them being state-specific. One may quote second order perturbation expansions based on determinants from selected references (CIPSI)^{14,15}, intermediate Hamiltonian dressing¹⁶, in the so-called shifted Bk technique¹⁷. These methods are not strictly size-consistent, the conditions to satisfy the strict separability of determinant-based expansions require to define sophisticated zero-order Hamiltonians¹⁸. Contracted perturbative expansions, which perturb the multideterminant zero-order wave function under the effect of linear combinations of outer-space determinants have also been proposed. One may quote the CASPT2 method^{19,20}, which uses a monoelectronic zero-order Hamiltonian, faces intruder state problems and is not size consistent, the NEVPT2 method²¹⁻²³ which uses a bi-electronic zero-order Hamiltonian (the Dyal's one²⁴) and is size consistent and intruder-state free, and the method from Werner²⁵, as well as the perturbation derived by Mukherjee *et al*²⁶⁻²⁸ from their MRCC formalism.

If the CASSCF wave function is considered as the counterpart of the single determinant reference the CASSDCI is the counterpart of the SDCI, with the same size-inconsistency defect, and the research of MRCEPA and MRCC has been the subject of intense methodological researches for about 20 years, without evident success. The cancellation of all unlinked terms in the MR expansion (i.e. a MRCEPA or MR(SC)²CI) formalism is not an easy task^{29,30}. If one lets aside the MRCC methods that attribute a specific role to a single reference³¹, a few state-specific strictly multi-reference

^{a)}Electronic mail: scemama@irsamc.ups-tlse.fr

CC methods have been proposed, one by one of the authors and collaborators¹, another one by Mukherjee and coworkers³², a third one in a Brillouin Wigner context^{33,34}. We return here on the first proposal which had only be tested on a single problem. We shall present briefly the method in section 2, then the principle of its implementation (section 3), followed by numerical illustrations of its accuracy (section 4). The last section will discuss the advantages of this formalism, its flexibility and possible extensions.

II. METHOD

A. Principle

Let us call $|I\rangle$ the reference determinants, the number of which will be called N . The reference space may be a CAS, but this is only compulsory if one wants to satisfy the strict-separability property. If not the method is applicable to incomplete model spaces as well. The projector on the model space is

$$\hat{P}_0 = \sum_I |I\rangle\langle I|. \quad (1)$$

Let us consider a zero-order wave function restricted to the model space,

$$|\Psi_0^m\rangle = \sum_I c_I^m |I\rangle. \quad (2)$$

This function may be either the eigenfunction of $\hat{P}_0 \hat{H} \hat{P}_0$,

$$\hat{P}_0 \hat{H} \hat{P}_0 |\Psi_0^m\rangle = E_0^m |\Psi_0^m\rangle, \quad (3)$$

or the projection of the eigenvector of the CASSDCI on the model space

$$|\Psi_0^m\rangle = \hat{P}_0 |\Psi_{\text{CASSDCI}}^m\rangle. \quad (4)$$

The CASSDCI wave function is written as

$$|\Psi_{\text{CASSDCI}}^m\rangle = \sum_I c_I^m |I\rangle + \sum_i c_i^m |i\rangle \quad (5)$$

where $|i\rangle$ are the Singles and Doubles (the determinants of the CASSDCI space which do not belong to the reference space). We want to follow a Jeziorski-Monkhorst³⁵ expression of the wave operator $\hat{\Omega}$ which is supposed to send from the zero-order wave function to the exact one

$$\hat{\Omega} |\Psi_0^m\rangle = |\Psi^m\rangle \quad (6)$$

as a sum of reference-dependent operators

$$\hat{\Omega} \hat{P}_0 = \sum_I \hat{\Omega}_I |I\rangle\langle I|. \quad (7)$$

Each of the $\hat{\Omega}_I$'s will take an exponential form

$$\hat{\Omega}_I = \exp(\hat{T}_I), \quad (8)$$

and each operator \hat{T}_I will be truncated to the single and double excitations, as one does in the CCSD formalism.

B. The multi-parentage problem and the extraction of guess values of the excitation amplitudes from the CASSDCI eigenvector

One may easily recognize that there exist some degrees of freedom in the determination of the wave operators. In the single reference CCSD expansion one searches for the amplitudes of the excitations sending from the reference Φ_0 to the singly and doubly excited determinants. One evaluates the amplitudes of the Triples and Quadruples as given by the action of \hat{T}^2 on Φ_0 , and the eigenequation is projected on each of the Singles and Doubles. If the number of Singles and Doubles is n , one may write a set of n coupled quadratic equations on the amplitudes. But it may be more convenient to guess a first evaluation of these amplitudes from the coefficients of the Singles and Doubles in the SDCI matrix, which may be done in a unique manner. From these amplitudes one may obtain a guess of the coefficients of the Triples and Quadruples and it is convenient (ensuring for instance a better convergence than solving coupled biquadratic equation) to write the process as an iterative dressing of the SDCI matrix, in the spirit of Intermediate Effective Hamiltonian formalism¹⁶.

In the multireference context one faces a genealogical problem, sometimes called the multiple-parentage problem. Actually for a state-specific formalism, one has only one coefficient for each of the singly and doubly excited determinants $|i\rangle$. In principle one may decide that this determinant is obtained from each of the references and one would write then

$$c_i^m = \sum_I d_{Ii}^m c_I^m \quad (9)$$

but one must find a criterion to define the N d_{Ii} amplitudes from the knowledge of a single coefficient. Returning to a perturbative estimate of the coefficients of the Singles and Doubles starting from Ψ_0^m , the first-order expression of these coefficients

$$c_i^{m(1)} = \frac{\langle \Psi_0^m | \hat{H} | i \rangle}{E_0^m - \langle i | \hat{H} | i \rangle} = \sum_I c_I^m \frac{\langle I | \hat{H} | i \rangle}{E_0^m - \langle i | \hat{H} | i \rangle} \quad (10)$$

suggests that the amplitudes of the excitation operators from the references to the Singles and Doubles might satisfy

$$\frac{d_{Ii}^m}{d_{Ji}^m} = \frac{\langle I | \hat{H} | i \rangle}{\langle J | \hat{H} | i \rangle}. \quad (11)$$

This scaling had been proposed in ref.¹. This condition may be expressed as

$$d_{Ii}^m = \lambda_i^m \langle I | \hat{H} | i \rangle \quad (12)$$

where the quantity λ_i^m is the inverse of an energy. Reinjecting this expression in Eq.(9) leads to

$$c_i^m = \lambda_i^m \sum_I c_I^m \langle I | \hat{H} | i \rangle, \quad (13)$$

which defines λ_i^m as

$$\lambda_i^m = \frac{c_i^m}{\langle \Psi_0^m | \hat{H} | i \rangle} \quad (14)$$

These are the key equations which define guess values of the amplitudes of the excitations leading from the references to the Singles and Doubles. Notice that we only consider amplitudes for the excitations which correspond to physical interactions, and since \hat{H} is at most bi-electronic, one only introduces single- and double-excitation operators. Finally, we can re-express the CASSDCI wave function as

$$|\Psi_{\text{CASSDCI}}^m\rangle = \sum_I c_I^m \left(1 + \sum_i d_{Ii}^m \hat{T}_{Ii} \right) |I\rangle \quad (15)$$

where

$$\hat{T}_{Ii}|I\rangle = |i\rangle. \quad (16)$$

C. Coefficients of the Triples and Quadruples

One may then generate the Triples and Quadruples $|\alpha\rangle$. Among them only those which interact with the Singles and Doubles (i.e. which are generated by the action of \hat{H} on the Singles and Doubles and which do not belong to the CASSDCI space) have to be considered. One may find the references with which they present either 3 or 4 differences in the occupation numbers of the molecular orbitals (MOs). These reference determinants may be called the *grand-parents* of $|\alpha\rangle$. The comparison between $|\alpha\rangle$ and each of its grand-parents $|I\rangle$ defines the excitation operator from $|I\rangle$ to $|\alpha\rangle$ as a triple or quadruple excitation

$$\hat{T}_{I\alpha}|I\rangle = |\alpha\rangle \quad (17)$$

which may be expressed in second quantization as the product of 4 (or 3) creation operators and 4 (or 3) annihilation operators

$$\hat{T}_{I\alpha} = a_q^\dagger a_p^\dagger a_n^\dagger a_m^\dagger a_e a_f a_g a_h \quad (18)$$

The creations run on active and virtual MOs, the annihilations run on active and inactive occupied MOs but the number of inactive indices among the creation and/or among the particles must be equal to 3 or 4, otherwise the determinant would belong to the CASSDCI space. Knowing the operator, it may be factorized as the product of two complementary double (or single) excitation operators in all possible manners (each double excitation keeping untouched the M_s value)

$$\hat{T}_{I\alpha} = \pm \hat{T}_{Ik} \hat{T}_{Il} = \pm \hat{T}_{Iv} \hat{T}_{Iu} = \dots \quad (19)$$

Then we may write the contribution to the coefficient of $|\alpha\rangle$ issued from the reference $|I\rangle$ as

$$d_{I\alpha}^m = \sum_{(k,l) \in (I \rightarrow \alpha)} \pm d_{Ik}^m d_{Il}^m \quad (20)$$

where $\{(k,l) \in (I \rightarrow \alpha)\}$ denotes the couples (k,l) for which $\hat{T}_{Ik} \hat{T}_{Il} = \pm \hat{T}_{I\alpha}$. The sign is governed by the permutation logics. Then one might write the coefficient c_α^m as

$$c_\alpha^m = \sum_I d_{I\alpha}^m c_I^m. \quad (21)$$

D. Dressing of the CASSDCI matrix

If one considers the eigenequation relative to $\langle i|$

$$\begin{aligned} \left(\langle i | \hat{H} | i \rangle - E^m \right) c_i^m + \sum_I \langle i | \hat{H} | I \rangle c_I^m + \sum_{j \neq i} \langle i | \hat{H} | j \rangle c_j^m \\ + \sum_\alpha \langle i | \hat{H} | \alpha \rangle c_\alpha^m = 0 \end{aligned} \quad (22)$$

one may decompose the last term

$$\begin{aligned} \sum_\alpha \langle i | \hat{H} | \alpha \rangle c_\alpha^m &= \sum_\alpha \langle i | \hat{H} | \alpha \rangle \sum_I d_{I\alpha}^m c_I^m \\ &= \sum_I \left(\sum_\alpha d_{I\alpha}^m \langle i | \hat{H} | \alpha \rangle \right) c_I^m \end{aligned} \quad (23)$$

Introducing the quantities

$$\langle i | \hat{\Delta}^m | I \rangle = \sum_\alpha d_{I\alpha}^m \langle i | \hat{H} | \alpha \rangle, \quad (24)$$

one may write the eigenequation (22) as

$$\begin{aligned} \left(\langle i | \hat{H} | i \rangle - E^m \right) c_i^m + \sum_I \left(\langle i | \hat{H} | I \rangle + \langle i | \hat{\Delta}^m | I \rangle \right) c_I^m \\ + \sum_{j \neq i} \langle i | \hat{H} | j \rangle c_j^m = 0 \end{aligned} \quad (25)$$

which suggests to treat the effect of the Triples and Quadruples as a column dressing of the CASSDCI matrix. A similar idea has been exploited in the single-reference CCSD context, which may be presented and managed as an iterative dressing of the column between the reference and the Singles and Doubles³⁶. The Coupled Cluster dressed CASSDCI Hamiltonian may be written as $\hat{P}_{\text{CASSDCI}} (\hat{H} + \hat{\Delta}^m) \hat{P}_{\text{CASSDCI}}$, which is non-Hermitian. Defining the projector on the Singles and Doubles as

$$\hat{P}_{\text{SD}} = \hat{P}_{\text{CASSDCI}} - \hat{P}_0, \quad (26)$$

$$\hat{P}_{\text{CASSDCI}} \hat{\Delta}^m \hat{P}_{\text{CASSDCI}} = \hat{P}_{\text{SD}} \hat{\Delta}^m \hat{P}_0 \quad (27)$$

one may define an equivalent Hermitian dressing $\hat{\Delta}^{m'}$ in the case where one considers the Hermitization of the dressed CASSDCI matrix to be desirable,

$$\langle i | \hat{\Delta}^{m'} | I \rangle = \langle I | \hat{\Delta}^{m'} | i \rangle = \langle i | \hat{\Delta}^m | I \rangle \quad (28)$$

provided that one introduces a diagonal dressing of the CASSDCI matrix

$$\langle I | \hat{\Delta}^{m'} | I \rangle = -\frac{1}{c_I^m} \left(\sum_i \langle I | \hat{\Delta}^{m'} | i \rangle c_i^m \right) \quad (29)$$

The diagonalization of the matrices $\hat{P}_{\text{CASSDCI}} (\hat{H} + \hat{\Delta}^m) \hat{P}_{\text{CASSDCI}}$ and $\hat{P}_{\text{CASSDCI}} (\hat{H} + \hat{\Delta}^{m'}) \hat{P}_{\text{CASSDCI}}$ will give the same desired eigenenergy and eigenvector

$$\hat{P}_{\text{CASSDCI}} (\hat{H} + \hat{\Delta}^m) \hat{P}_{\text{CASSDCI}} |\Psi_{\text{CC}}^m\rangle = E_{\text{CC}}^m \hat{P}_{\text{CASSDCI}} |\Psi_{\text{CC}}^m\rangle \quad (30)$$

$$\hat{P}_{\text{CASSDCI}} (\hat{H} + \hat{\Delta}^{m'}) \hat{P}_{\text{CASSDCI}} |\Psi_{\text{CC}}^m\rangle = E_{\text{CC}}^m \hat{P}_{\text{CASSDCI}} |\Psi_{\text{CC}}^m\rangle \quad (31)$$

Of course the process has to be iterated, the resulting eigenvector defines new coefficients on both the references and the Singles and Doubles, which lead to new amplitudes, new evaluations of the coefficients of the Triples and Quadruples, new dressings. Since the eigenvectors of the dressed matrices are identical, the two formulations, Hermitian or non-Hermitian, converge to the same solution. The converged solutions are the MRCCSD energy and the MRCCSD amplitudes, which define the exponential wave operator.

III. IMPLEMENTATION

The proposed algorithm was implemented in the *Quantum Package*³⁷, an open-source series of programs developed in our laboratory. The bottleneck of this algorithm is the determinant comparisons needed to determine the excitation operators and phases during the reconstruction of the genealogy of the $|\alpha\rangle$'s. This was made possible thanks to a very efficient implementation of Slater-Condon's rules³⁸.

A. General structure

At each iteration step, one first assigns the values of the λ_i^m parameters obtained from the eigenvector of the (dressed) CASSDCI matrix according to equation (14). From these parameters λ_i^m the amplitudes of the single and double excitations are uniquely defined. Then one loops on the Singles and Doubles $|i\rangle$. On each of them one reapplies the excitation operators to generate the $|\alpha\rangle$'s. Those which belong to the CASSDCI space are eliminated. The parents of $|\alpha\rangle$ (that are all the Singles and Doubles $|k\rangle$'s such that $\langle \alpha | \hat{H} | k \rangle \neq 0$) are generated. If one of the $|k\rangle$'s has already been considered in the loop on the $|i\rangle$'s ($k < i$), this $|\alpha\rangle$ has been already generated and taken into account and must not be double counted.

While generating the parents of $|\alpha\rangle$, its interactions with them, $\langle k | \hat{H} | \alpha \rangle$, are stored. At this step, the reference grand-parents $|I\rangle$ are identified as having 3 or 4 differences with $|\alpha\rangle$. Then, the excitation operator leading from $|I\rangle$ to $|\alpha\rangle$ is expressed in all possible manners as products of two complementary single or double excitations. For each couple of complementary excitations, the product of the amplitudes is accumulated to compute $d_{I\alpha}^m$ according to equation (20). Finally, the product of $\langle k | \hat{H} | \alpha \rangle$ with $d_{I\alpha}^m$ is accumulated in $\langle k | \hat{\Delta}^m | I \rangle$ for each parent $|k\rangle$ of $|\alpha\rangle$ according to equation (24). Once the loop on the $|i\rangle$'s is done, all the $|\alpha\rangle$'s have been generated, and the column dressing is completed. Then, in order to fit with a symmetric diagonalization technique, one symmetrizes the dressing as mentioned in the preceding section (equations (28) and (29)). The dressed CASSDCI matrix is diagonalized and the process is repeated up to convergence of the calculated dressed energy. From the computational point of view, this process requires the storing of the dressing columns which scales as $N \times (n_{\text{occ}} n_{\text{virt}})^2$ where N is the number of determinants in the reference, n_{occ} and n_{virt} are respectively the number of occupied and virtual MOs. This amount of memory is reasonable, and does not represent a bottleneck for the present applications. Regarding the CPU time, the costly part concerns the handling of the $|\alpha\rangle$'s which scales as $(n_{\text{occ}} n_{\text{virt}})^4$. Nevertheless, the process is perfectly parallelizable as all the work done with the $|\alpha\rangle$'s generated from $|i\rangle$ does not depend on the other $|i\rangle$'s.

B. Practical issues

The definition of λ_i^m can lead to numerical instabilities when $\langle \Psi_0^m | \hat{H} | i \rangle$ is small. Nevertheless, in such cases the contribution of $|i\rangle$ to the post-CAS correlation energy is also small, suggesting that one might use a perturbative estimate of λ_i^m . In practice, we use the perturbative λ_i according to two different criteria. The first one concerns the ratio of the variational coefficient c_i^m (obtained at a given iteration) over its perturbative estimate (see (10)). If $\frac{c_i^{m(1)}}{c_i^m} \notin [0, 0.5]$ then the amplitudes involving $|i\rangle$ are determined using the perturbative $\lambda_i^{m(\text{pert})}$ defined as

$$\lambda_i^{m(\text{pert})} = \frac{1}{E_0^m - \langle i | \hat{H} | i \rangle} \quad (32)$$

In such situations the coefficient c_i^m is not determined by its interaction with the reference determinants, but comes from higher-order effects. The second criterion concerns the absolute value of each of the d_{Ii}^m defined according to (12). If any of these terms calculated with the λ_i^m obtained from the variational calculation (see (14)) is larger than 0.5, the perturbative $\lambda_i^{m(\text{pert})}$ is used to determine the amplitudes $d_{Ii}^{m(\text{pert})}$ defined as

$$d_{Ii}^{m(\text{pert})} = H_{Ii} \lambda_i^{m(\text{pert})} \quad (33)$$

and the working amplitudes d_{Ti}^m are set to $d_{Ti}^{m(\text{pert})}$. This condition avoids numerical instabilities occurring when both c_i^m and $\langle \psi_0^m | \hat{H} | i \rangle$ are small, and allows us the control of the maximum value of the amplitudes. As soon as along the iterations one of the $|i\rangle$'s fulfills one of these criteria, it will be treated perturbatively in the following iterations. This precaution avoids significant oscillations due to back and forth movements from perturbative to variational treatment of the λ_i^m . The numerically observed residual oscillations are of the order of magnitude of $10^{-6} E_h$, which may certainly be attributed to the non linear character of the numerical algorithm. Nevertheless, the order of magnitude of the residual oscillations is much smaller than the chemical and even spectroscopic accuracy.

IV. NUMERICAL TEST STUDIES

We decided to test the accuracy and robustness of the method on a series of benchmarks, some of which have been used in the evaluations of other MRCC proposals and of alternative MR approaches. They essentially concern model problems, especially bond breaking problems or the treatment of degenerate situations. They require to use a CAS with either two electrons in two MOs or four electrons in four MOs. In all cases the method converged in a few iterations. A systematic comparison is made with FCI estimates, either taken from the literature or obtained from a CIPSI type variation+perturbation calculation^{14,15} where the perturbative residue is about $-6 mE_h$. Of course the CASSDCI is already a rather sophisticated treatment, which takes into account, although in a size-inconsistent manner, the leading correlation effects, both the non-dynamical part in the CAS and the dynamical part in the SDCI step. One may expect that the improvement brought by the MRCC treatment will be significant when the number of important inactive double excitations is large.

In order to have a global view of the performance of the here-proposed algorithm, we report for each calculation (except the symmetric dissociation of the water molecule) potential energy curves, the error to FCI estimate of our MRCCSD algorithm together with the CASSDCI. Tables showing the error with respect to the FCI estimate of the MRCCSD and CASSDCI are also presented, complemented by the total energies of the FCI estimate. The non-parallelism error (NPE) is here calculated as the difference between the minimum and maximum error to the FCI estimate. The spectroscopic constants are obtained from an accurate fit of the obtained potential energy curves with a generalized Morse potential representation. The spectroscopic constants reported here are the equilibrium distance R_{eq} in Å, the frequency k_{eq} in $E_h/\text{Å}^2$ and the atomization energy D_e in kcal/mol.

All the calculations were performed with the Quantum Package³⁷, an open-source series of programs developed in our group.

A. Single-bond breakings

The treatment of the breaking of a single bond in principle requires only a CASSCF zero-order treatment including two electrons in two MOs. We have considered three problems of that type.

Bond breaking of the F_2 molecule

The F_2 molecule is a paradigmatic molecule since it is a case where the dynamical correlation brings a crucial contribution to the bonding. Despite the closed shell character of the wave function in the equilibrium region the single reference Hartree-Fock (HF) solution is unbound (by 18 kcal/mol) with respect to the restricted open shell HF solution of the fluorine atoms. The 2-electron in 2-MO CASSCF treatment binds the molecule by 18 kcal/mol, but the experimental binding energy is much larger (39 kcal/mol). Going to a full valence CASSCF (14 electrons in 10 MOs) does not bring any improvement. The role of the dynamical correlation has been extensively studied and may be seen as a dynamic response of the lone pair electrons to the fluctuation of the electric field created by the two electrons of the σ bond^{39,40}. The concept of orbital breathing has been proposed to express the fact that the orbitals of the lone pairs tend to become more diffuse on the negative center and more contracted on the positive center in the ionic valence-bond (VB) components of the CAS. These dynamic relaxation processes can only take place if one uses non-minimal basis sets.

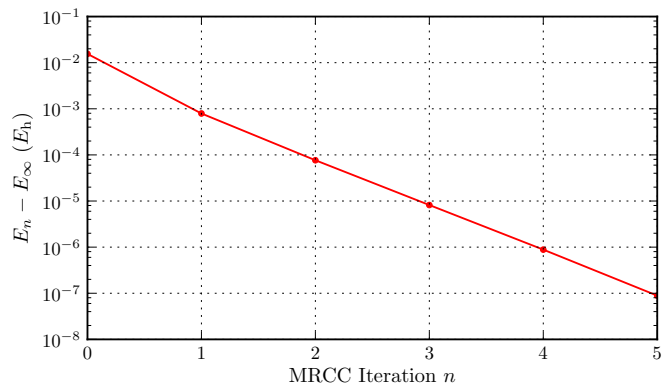


FIG. 1. F_2 molecule at $R=1.45$ Å, cc-pVDZ basis set. Convergence of the MRCCSD energy along the iterations.

The calculations of F_2 were obtained in the cc-pVDZ basis set⁴¹ keeping the $1s$ electrons frozen, and accurate FCI estimates are taken from the work of Bytautas *et al*⁴². Figure 1 shows an exponential convergence of the energy along the MRCC iterations. The here-reported calculation, performed in a medium size basis set, does not afford a sufficient flexibility to reach the experimental binding energy (the estimated FCI binding energy in this basis is $D_e=28.3$ kcal/mol). The potential energy curves

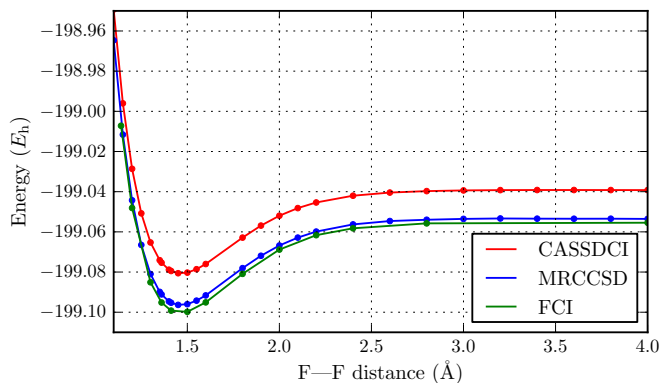


FIG. 2. Potential energy curves of the F_2 molecule, cc-pVDZ basis set.

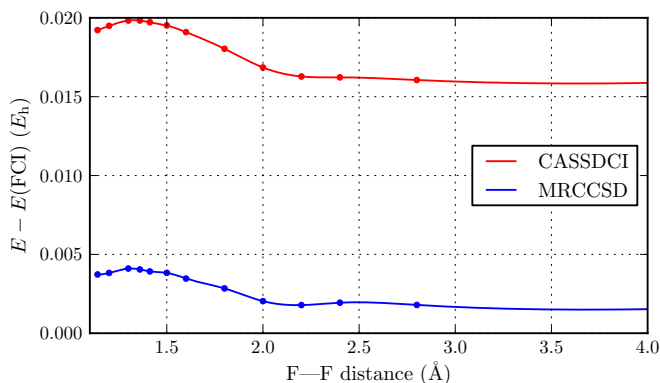


FIG. 3. F_2 molecule, cc-pVDZ basis set. Errors with respect to the FCI estimate as a function of the F—F distance.

and the error to FCI estimate are reported, respectively in Figure 2 and Figure 3, and the estimated FCI values together with the error of the MRCCSD and CASSDCI calculations appear in Table I. The average error is reduced by a factor close to 6, and the NPE is only reduced by 40% by the MRCCSD calculations.

The C—C bond breaking in ethane

This calculation is performed in the 6-31G basis set, keeping the 1s electrons frozen. The geometrical parameters are given in Table II. The potential energy curves are reported in Figure 4 and the errors with respect to the FCI estimate appear in Figure 5. These data show that the error with respect to the FCI energy is greatly reduced by a factor of 6 in average. According to Table III, the NPE goes from 2.01 mE_h to 1.32 mE_h for respectively the CASSDCI and MRCCSD approaches. Concerning the spectroscopic constants, the impact of the CC treatment is modest but goes in the right direction.

R (Å)	$E_{\text{CASSDCI}} - E_{\text{FCI}}$	$E_{\text{MRCCSD}} - E_{\text{FCI}}$	FCI estimate
1.14	19.223	3.726	-199.007 18
1.20	19.495	3.823	-199.048 11
1.30	19.825	4.102	-199.085 10
1.36	19.829	4.045	-199.095 17
1.41193	19.721	3.920	-199.099 20
1.50	19.518	3.830	-199.099 81
1.60	19.094	3.466	-199.095 10
1.80	18.038	2.843	-199.080 90
2.0	16.850	2.034	-199.068 82
2.2	16.280	1.783	-199.061 65
2.40	16.225	1.936	-199.058 23
2.80	16.055	1.794	-199.055 77
8.00	16.241	1.893	-199.055 45
R_{eq}	1.466	1.465	1.460
k_{eq}	0.730	0.739	0.795
D_e	26.01	26.91	28.31

TABLE I. F_2 molecule, cc-pVDZ basis set. Total energies are given in E_h , and the energy differences are given in mE_h .

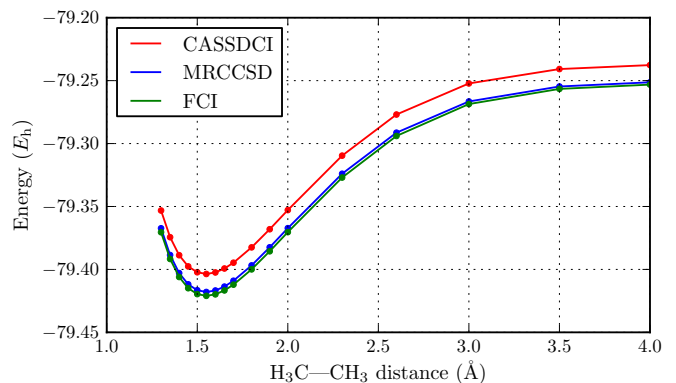


FIG. 4. Ethane molecule, 6-31G basis set. Potential energy curves along the C—C bond stretching.

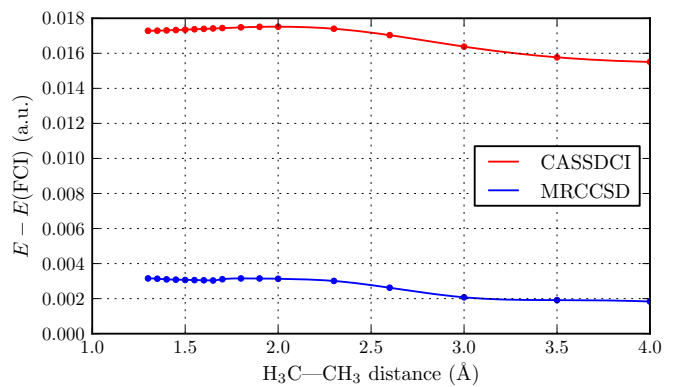


FIG. 5. Ethane molecule, 6-31G basis set. Errors with respect to the FCI estimate as a function of the C—C distance.

Geometrical parameters	C ₂ H ₆	C ₂ H ₄
C—H	1.103 Å	1.089 Å
C—C	1.550 Å	1.335 Å
H—C—C	111.2°	120.0°
H—C—H	107.6°	120.0°
H—C—C—H	180.0°	180.0°

TABLE II. Geometries used for ethane and ethylene.

R (Å)	$E_{\text{CASSDCI}} - E_{\text{FCI}}$	$E_{\text{MRCCSD}} - E_{\text{FCI}}$	FCI estimate
4.00	15.508	1.834	-79.253 166
3.50	15.770	1.915	-79.256 574
3.00	16.379	2.074	-79.268 617
2.60	17.037	2.622	-79.293 972
2.30	17.402	3.009	-79.326 999
2.00	17.519	3.134	-79.370 376
1.90	17.510	3.150	-79.385 598
1.80	17.482	3.152	-79.399 969
1.70	17.442	3.106	-79.412 107
1.65	17.419	3.035	-79.416 695
1.60	17.395	3.046	-79.419 813
1.55	17.371	3.055	-79.420 987
1.50	17.347	3.062	-79.419 613
1.45	17.326	3.083	-79.414 941
1.40	17.306	3.099	-79.406 030
1.35	17.291	3.135	-79.391 701
1.30	17.284	3.153	-79.370 480
R_{eq}	1.549	1.550	1.550
k_{eq}	1.018	1.017	1.015
D_{e}	104.52	104.99	105.75

TABLE III. Ethane molecule, 6-31G basis set. The FCI estimate is the CIPSI calculation. Total energies are given in E_{h} , and the energy differences are given in $\text{m}E_{\text{h}}$.

The rotation of the ethylene molecule around its C—C bond

This twisting breaks the π bond. The calculation is performed in the 6-31G basis set at the geometry given in Table II, keeping the $1s$ electrons frozen. The occupied MOs in the inactive space involve 10 electrons, and despite the modest size of the basis set one may expect a significant size-consistence defect of the CASSDCI results, since they miss the repeatability of inactive double excitations on the SD determinants. The potential energy curve along the angle of rotation is reported in Figure 6 and the error to the FCI estimate is reported in Figure 7. From these data it appears that the global shape of the potential energy curve obtained using the CC treatment is more parallel to the FCI curve than using the CASSDCI approach. From Table IV, one ob-

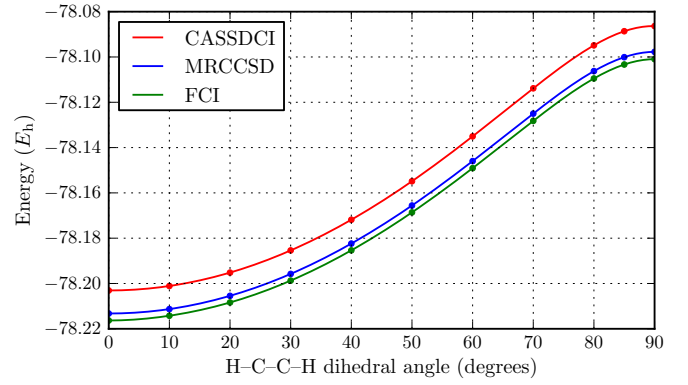


FIG. 6. Ethylene molecule, 6-31G basis set. Energy as a function of the rotation around the C—C bond.

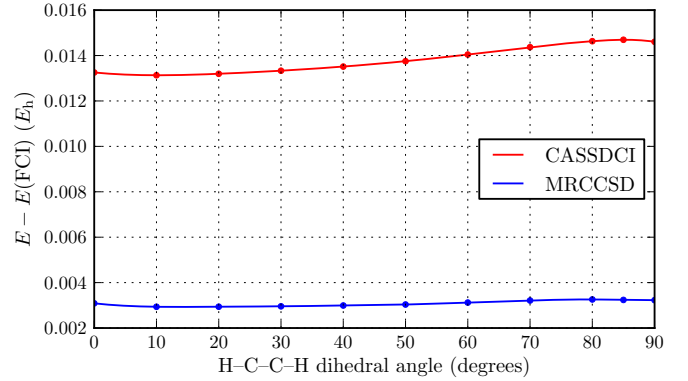


FIG. 7. Ethylene molecule, 6-31G basis set. Errors with respect to the FCI estimate as a function of the rotation around the C—C bond.

serves that the error with respect to the FCI estimate is reduced by a factor of 6 when going from CASSDCI to MRCCSD. Also, the NPE is also reduced from $1.6 \text{ m}E_{\text{h}}$ to $0.3 \text{ m}E_{\text{h}}$.

Angles (degrees)	$E_{\text{CASSDCI}} - E_{\text{FCI}}$	$E_{\text{MRCCSD}} - E_{\text{FCI}}$	FCI estimate
0	13.255	2.935	-78.216 340
10	13.132	2.935	-78.214 241
20	13.196	2.938	-78.208 391
30	13.331	2.955	-78.198 732
40	13.513	2.991	-78.185 373
50	13.750	3.035	-78.168 619
60	14.043	3.120	-78.149 094
70	14.368	3.212	-78.128 205
80	14.631	3.258	-78.109 498
85	14.694	3.237	-78.103 326
90	14.605	3.227	-78.100 966

TABLE IV. Rotation of the ethylene molecule, 6-31G basis set. The FCI estimate is the CIPSI calculation. Total energies are given in E_{h} , and the energy differences are given in $\text{m}E_{\text{h}}$.

B. Two-bond breakings

Three systems have been treated using a CAS with four electrons in 4 active MOs. Two of them concern the simultaneous breaking of two bonds.

Breaking of the C=C double bond of ethylene

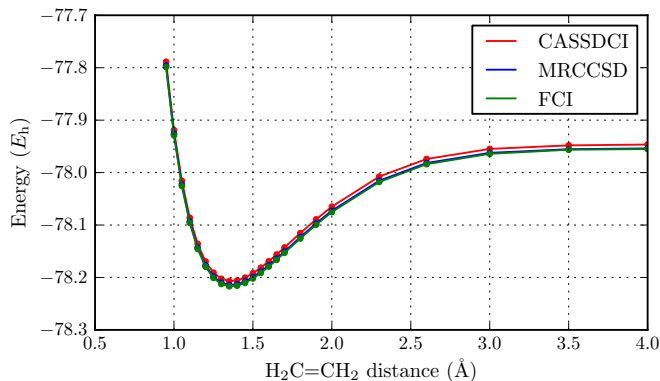


FIG. 8. Potential energy curves of the ethylene molecule, 6-31G basis set.

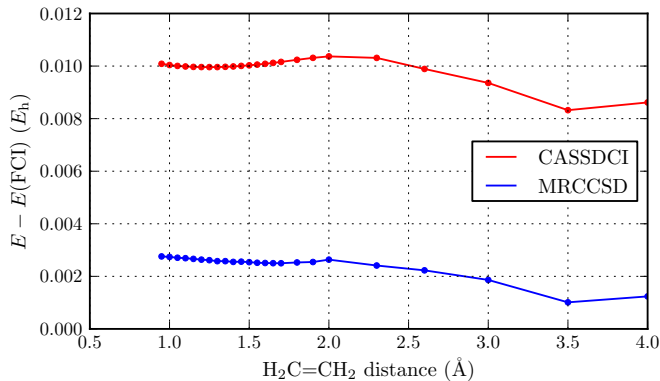


FIG. 9. Potential energy curves of the ethylene molecule, 6-31G basis set. Errors with respect to the FCI estimate as a function of the C—C distance.

The dissociation of the ethylene molecule by breaking the double bond was studied in the 6-31G basis set, with the geometry given in Table II. We report the potential energy curves in Figure 8, and the error with respect to the FCI estimate in Figure 9. The corresponding values appear in Table V. Again, the error to estimated FCI energy is reduced by a factor of 4, but the NPE is reduced only by 20% with the CC treatment.

Two-bond breaking in H₂O

This is a rather well known test problem for MRCC methods. The calculation is done with the cc-pVDZ basis

R (Å)	$E_{\text{CASSDCI}} - E_{\text{FCI}}$	$E_{\text{MRCCSD}} - E_{\text{FCI}}$	FCI estimate
1.20	9.962	2.635	-78.179 508
1.25	9.960	2.614	-78.200 805
1.30	9.961	2.578	-78.212 507
1.35	9.971	2.578	-78.216 869
1.40	9.985	2.549	-78.215 666
1.45	10.006	2.558	-78.210 313
1.50	10.028	2.539	-78.201 918
1.55	10.055	2.517	-78.191 365
1.60	10.085	2.507	-78.179 345
1.65	10.121	2.500	-78.166 404
1.70	10.158	2.498	-78.152 957
1.80	10.238	2.528	-78.125 775
1.90	10.313	2.545	-78.099 562
2.00	10.368	2.635	-78.075 294
2.30	10.310	2.411	-78.017 944
2.60	9.890	2.228	-77.983 952
3.00	9.358	1.863	-77.964 220
3.50	8.321	1.011	-77.956 421
4.00	8.616	1.237	-77.955 127
R_{eq}	1.362	1.362	1.362
k_{eq}	2.043	2.039	2.042
D_e	163.48	163.54	164.47

TABLE V. Dissociation of the ethylene molecule, 6-31G basis set. The FCI estimate is the CIPSI calculation. Total energies are given in E_h , and the energy differences are given in mE_h .

set at five different geometries obtained from the equilibrium geometry ($R_e=1.84345$ Å, and $\angle_{\text{HOH}} = 110.6^\circ$), in order to compare with the values of the literature.⁴³ The results appear in Table VI. The benefit of the MRCCSD with respect to the CASSDCI treatment is significant : the maximum error is 1.4 mE_h , better than the 6.4 mE_h given by the Mk-MRCC treatment. This improvement may be due to the here-proposed treatment of the amplitudes responsible for potential divergences. The NPE goes from 2 mE_h to 0.7 mE_h when the CC treatment is applied.

R (Å)	$E_{\text{CASSDCI}} - E_{\text{FCI}}$	$E_{\text{Mk}} - E_{\text{FCI}}$	$E_{\text{MRCCSD}} - E_{\text{FCI}}$	FCI
1 R_e	4.923	2.909	1.407	-76.241860
1.5 R_e	4.674	4.817	1.248	-76.072348
2.0 R_e	3.665	6.485	0.855	-75.951665
2.5 R_e	3.097	5.672	0.763	-75.917991
3.0 R_e	2.959	3.987	0.845	-75.911946

TABLE VI. Symmetric dissociation of the water molecule, cc-pVDZ basis set. The FCI total energy⁴⁴ is given in E_h , and the deviations to this reference are given in mE_h . Comparison with Mukherjee's state specific MRCC values ($E_{\text{Mk}} - E_{\text{FCI}}$) obtained from Ref.⁴³.

V. PROPERTIES

A. Internal decontraction

The method is internally decontracted. The coefficients of the references as well as those of the Singles and Doubles change along the iterations. If the reference space is a valence CAS, treating the non-dynamical correlation effects, the method takes care of the impact of the dynamical correlation on the non-dynamical part. The phenomenon is especially important in magnetic systems where the dynamical charge polarization effects increase dramatically the weight of the ionic Valence Bond components, diminishing severely the effective energy of these components.⁴⁰ This effect is already present in the CASSDCI calculation but the MRCCSD treatment eliminates the size consistency defect and slightly improves the quality of the projection of the wave function on the CAS.

B. Size consistence

The method does not introduce any unlinked diagram, and is therefore size-consistent. A proof of strict separability has been given in the original presentation of the method¹. It requires that in the splitting into two subsystems A and B the active and inactive MOs are localized on one of the two subsystems A or B. Actually, as occurs for the Mk-MRCC formalism, the method is not invariant with respect to the unitary transformation of the MOs in their class (inactive occupied, active, inactive virtual). This dependence will be studied in a future work, but the error to FCI being small we do not expect a strong dependence on the MO definition. As was shown in the study of bond breakings the asymptotic size-consistency error (which is demonstrated to be zero when localized MOs are used) is negligible in a basis of symmetry-adapted MOs.

C. Eigenfunction of \hat{S}^2

The here-proposed method does not provide an eigenfunction of \hat{S}^2 as we consider only the determinants that are connected by an application of \hat{H} to the determinants belonging to the CAS. This treatment does not include higher excitations which will generate the full space associated with a given space part. Along all the performed calculations on singlet states, the order of magnitude of the expectation value of \hat{S}^2 calculated on both the CASSDCI and the projected MRCCSD wave functions never exceeded 10^{-3} . A future work will present a solution working with the same restricted space but providing a strict eigenfunction of \hat{S}^2 .

VI. PROSPECTS

The formalism presented here allows us to conceive two main types of extensions for further work. The first one concerns the reduction of the computational cost of the method through various approximations, in order to target more realistic systems. From a methodological point of view, a refined treatment of the excited states deserves to be considered.

A. Computational cost

The method is extremely flexible, either on the choice of the reference space and/or of the excitations from it. One may partition the Singles and Doubles in terms of excitation classes. For instance the most numerous purely inactive excitations (2 holes, 2 particles) can be treated in a contracted manner, leading to a diagonal shift of the CASSDCI. Another possibility consists in omitting this class of excitation which does not contribute significantly to the vertical energy differences, as exploited in the DDCI framework⁴⁵. Then, one may exponentialize the semi active excitations and make the DDCI method size consistent. As the theory is determinant based, one can take advantage of this flexibility to realize a CIPSI like selection of the dominant contributions of both the references and the single and double excitations. Further works will investigate the various possibilities such as the combination of MRCC with perturbation theory.

B. Excited states

The method is applicable to excited states using several approaches. The formalism being state specific, the dressing technique of the CI matrix can be applied to any state dominated by the reference determinants, as long as a state following procedure is applied. For states belonging to the same symmetry, the resulting eigenvectors will not be strictly orthogonal but might be orthogonalized *a posteriori*. Another possibility consists in a state average procedure where the amplitudes are obtained from the values of the quantities λ_i averaged over all desired eigenstates:

$$\lambda_i = \frac{\sum_m \lambda_i^m (c_i^m)^2}{\sum_m (c_i^m)^2} \quad (34)$$

If one refers to the perturbative expression of the first order coefficients,

$$\lambda_i^m \approx \frac{1}{E_0^m - \langle i | \hat{H} | i \rangle} \quad (35)$$

this approximation should be relevant when the states are close enough in energy.

A recent paper⁴⁶ has proposed a generalization of this approach to the simultaneous treatment of several states

of the same symmetry. The basic ideas are the same, except for the fact that the extraction of the amplitudes is more complex. The method requires to partition the reference space into a main and an intermediate model spaces, in the spirit of the intermediate Hamiltonian formalism. This proposal will be tested in a further work.

VII. CONCLUSION

This work shows the relevance of a solution previously proposed to the problem of the multiple parentage faced by all Multi-Reference treatments, as soon as the number of targeted vectors is lower than the number of References. The proposed MRCC algorithm is simple. It only introduces two-body excitation operators and the number of amplitudes to be determined is reduced to the very minimum. It proceeds through an iterative dressing of the MRCI matrix, formulated in terms of a standard eigenvalue equation. It is parallelizable in the most expensive step (the generation of the coefficients of the Triples and Quadruples). It is entirely decontracted and may be applied to excited states. For the list of benchmark studies we have performed, the results are extremely encouraging. The present version is state-specific but the principles of extension to a multi-root version have been formulated. This work actually opens into several directions, which have to be explored in the future. The reduction of the computational cost might be done using several approximations involving the selection of the references and/or Singles and Doubles according to various criteria. Furthermore, the excited states can be treated using different approaches, all of them being compatible with the here-proposed formalism.

On a different perspective, the multiple parentage problem, which was faced here in the purpose of building a logically consistent computational tool to go in the direction of the exact solution, also concerns the building of rational valence-only effective Hamiltonians. In such an approach, the idea is to map the information coming from a sophisticated treatment into a minimal effective Hamiltonian, the parameters of which should be as physically meaningful as possible.⁴⁷ We believe that the solution we proposed to the multiple parentage problem offers a rational solution to this reduction of information. This remark illustrates the intrinsic link between the two main tasks of Quantum Chemistry, namely the production of physically grounded interpretative models on one hand and the conception of rigorous computational tools.

- ¹J. Meller, J. P. Malrieu, and R. Caballol, *J. Chem. Phys.* **104**, 4068 (1996).
- ²J. Goldstone, *Proc. Roy. Soc. A* **239**, 267 (1957).
- ³H. P. Kelly and M. A. Sessler, *Phys. Rev.* **132**, 2091 (1963).
- ⁴H. P. Kelly, *Phys. Rev.* **134**, A1450 (1964).
- ⁵W. Meyer, *Int. J. Quantum Chem.* **5**, 341 (1971).
- ⁶W. Meyer, *J. Chem. Phys.* **58**, 1017 (1973).
- ⁷W. Meyer, *Theor. Chim. Acta* **35**, 277 (1974).
- ⁸J. P. Daudey, J. L. Heully, and J. P. Malrieu, *J. Chem. Phys.* **99**, 1240 (1993).
- ⁹F. Coester, *Nucl. Phys.* **7**, 421 (1958).
- ¹⁰F. Coester and H. Kümmel, *Nucl. Phys.* **17**, 477 (1960).
- ¹¹J. Čížek, *J. Chem. Phys.* **45**, 4256 (1966).
- ¹²R. J. Bartlett, J. Watts, S. Kucharski, and J. Noga, *Chem. Phys. Lett.* **165**, 513 (1990).
- ¹³B. H. Brandow, *Rev. Mod. Phys.* **39**, 771 (1967).
- ¹⁴B. Huron, P. Rancurel, and J. P. Malrieu, *J. Chem. Phys.* **58**, 5745 (1973).
- ¹⁵S. Evangelisti, J. P. Daudey, and J. P. Malrieu, *Chem. Phys.* **75**, 91 (1983).
- ¹⁶J. P. Malrieu, P. Durand, and J. P. Daudey, *J. Phys. A : Math. Gen.* **18**, 809 (1985).
- ¹⁷B. Kirtman, *J. Chem. Phys.* **75**, 798 (1981).
- ¹⁸J. L. Heully, J. P. Malrieu, and A. Zaitsevskii, *J. Chem. Phys.* **105**, 6887 (1996).
- ¹⁹K. Andersson, P. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, *J. Phys. Chem.* **94**, 5483 (1990).
- ²⁰K. Andersson, P. Malmqvist, and B. O. Roos, *J. Chem. Phys.* **96**, 1218 (1992).
- ²¹C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, and J. P. Malrieu, *J. Chem. Phys.* **114**, 10252 (2001).
- ²²C. Angeli, R. Cimiraglia, and J. P. Malrieu, *Chem. Phys. Lett.* **350**, 297 (2001).
- ²³C. Angeli, R. Cimiraglia, and J. P. Malrieu, *J. Chem. Phys.* **117**, 9138 (2002).
- ²⁴K. G. Dyall, *J. Chem. Phys.* **102**, 4909 (1995).
- ²⁵P. Celani and H. J. Werner, *J. Chem. Phys.* **112**, 5546 (2000).
- ²⁶P. Ghosh, S. Chattopadhyay, D. Jana, and D. Mukherjee, *Int. J. Mol. Sci.* **3**, 733 (2002).
- ²⁷U. S. Mahapatra, B. Datta, and D. Mukherjee, *Chem. Phys. Lett.* **299**, 42 (1999).
- ²⁸A. Sen, S. Sen, P. K. Samanta, and D. Mukherjee, *J. Comput. Chem.* **36**, 670 (2015).
- ²⁹P. G. Szalay, T. Müller, G. Gidofalvi, H. Lischka, and R. Shepard, *Chem. Rev.* **112**, 108 (2012).
- ³⁰D. I. Lyakh, M. Musiał, V. F. Lotrich, and R. J. Bartlett, *Chem. Rev.* **112**, 182 (2012).
- ³¹N. Oliphant and L. Adamowicz, *J. Chem. Phys.* **94**, 1229 (1991).
- ³²U. S. Mahapatra, B. Datta, and D. Mukherjee, *Mol. Phys.* **94**, 157 (1998).
- ³³J. Mášik and I. Hubač, in *Adv. in Quant. Chem.* (Academic Press, 1998) pp. 75–104.
- ³⁴I. Hubač, J. Pittner, and P. Čársky, *J. Chem. Phys.* **112**, 8779 (2000).
- ³⁵B. Jeziorski and H. J. Monkhorst, *Phys. Rev. A* **24**, 1668 (1981).
- ³⁶I. Nebot-Gil, J. Sánchez-Mariñ, J. P. Malrieu, J. L. Heully, and D. Maynau, *J. Chem. Phys.* **103**, 2576 (1995).
- ³⁷A. Scemama, E. Giner, T. Applencourt, G. David, and M. Caffarel, “Quantum package v0.6,” (2015), doi:10.5281/zenodo.30624.
- ³⁸A. Scemama and E. Giner, *ArXiv e-prints [physics.comp-ph]*, 1311.6244 (2013).
- ³⁹P. Hiberty, J. Flament, and E. Noizet, *Chem. Phys. Lett.* **189**, 259 (1992).
- ⁴⁰J. P. Malrieu, N. Guihéry, C. J. Calzado, and C. Angeli, *J. Comput. Chem.* **28**, 35 (2007).
- ⁴¹T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- ⁴²L. Bytautas, T. Nagata, M. S. Gordon, and K. Ruedenberg, *J. Chem. Phys.* **127**, 164317 (2007).
- ⁴³S. Das, D. Mukherjee, and M. Kállay, *J. Chem. Phys.* **132**, 074103 (2010).
- ⁴⁴J. Olsen, P. Jørgensen, H. Koch, A. Balkova, and R. J. Bartlett, *J. Chem. Phys.* **104**, 8007 (1996).
- ⁴⁵J. Miralles, O. Castell, R. Caballol, and J. P. Malrieu, *Chem. Phys.* **172**, 33 (1993).
- ⁴⁶J. P. Malrieu, *Mol. Phys.* **111**, 2451 (2013).
- ⁴⁷B. Pradines, N. Suaud, and J. P. Malrieu, *J. Phys. Chem. A* **119**, 5207 (2015).